

Enthalpy Relaxation Kinetics of the $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ Supercooled Liquid Close to the Glass Transition

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ABSTRACT

Isothermal relaxation study of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ bulk metallic glass forming alloy was performed using Differential Scanning Calorimetry (DSC) in the glass transition and the supercooled liquid region. An experimental method of enthalpy relaxation was developed to study the isothermal relaxation kinetics below the glass transition region. Results revealed that the enthalpy relaxes in an Arrhenius fashion. The activation energy obtained from the Arrhenius fit is comparable to the activation energy required for the diffusion of the medium size atoms. This suggests that the solid-state diffusion governs the enthalpy relaxation process. The stretching exponents for the relaxation are close to unity, which indicates that the alloy is a rather strong glass former.

INTRODUCTION

Modern bulk metallic multi-component alloys show excellent glass forming ability [1-3]. The recently found Vitreloy 106a with a composition of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ (at%) is a revision in a series of Vitreloy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{13.5}\text{Ni}_{10}\text{Be}_{22.5}$, $\text{Zr}_{46.75}\text{Ti}_{8.8}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, $\text{Zr}_{52.5}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$, and $\text{Zr}_{57}\text{Cu}_{15.4}\text{Ni}_{12.6}\text{Al}_{10}\text{Nb}_5$. This relatively new bulk metallic glass (BMG) forming alloy has improved glass forming ability (GFA) compared to the neighboring compositions in the Zr-Nb-Cu-Ni-Al alloy with small changes in the Zr-Nb and Cu-Ni-Al contents [4]. This alloy does not contain beryllium, has large supercooled liquid region and can be processed by the critical cooling rate of less than 10K/s (as low as 1.75K/s) [5]. This paper studies the enthalpy relaxation kinetics of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ in the vicinity of the glass transition temperature (T_g). Till date, relaxation in the vicinity of T_g is not described by a single relaxation time. Rather distributions of relaxation time are required to represent experimental data [6].

EXPERIMENTAL METHOD

In this study of the $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ alloy isothermal measurements were done in the glassy region, calorimetric glass transition region as well as supercooled liquid region using Perkin Elmer Pyris Differential Scanning Calorimeter (DSC). The 90 to 170 mg specimens used for the DSC were cut from the as prepared strip of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ cast from an ingot that was melted from highly pure metals. All the samples were first subjected to a preannealing treatment. Preannealing requires heating the samples above the glass transition temperature at a rate of 0.33 K/s and allowing them to cool back to room temperature at the same rate to give all samples the same thermal history. Prior to and during each experiment the DSC was purged with 99.999% argon. Indium and Zinc were used as a low and high calibration standard respectively

during calibration. In all the experiments, samples were heated to the assigned isothermal temperatures with a rate of 1 K/s followed by cooling to room temperature. A base line run was carried out immediately after the sample run under exactly the same thermal conditions as sample run.

RESULTS

As $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ has better resistance to crystallization in its supercooled and glass transition region [5], it is possible to study relaxation from the glassy state into the supercooled liquid state. Measurements of isothermal enthalpy relaxation experiments of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ carried out below the glass transition temperature shows that sample gets isothermally relaxed from the glassy state into the supercooled liquid state as shown in figure 1. In our experiments it is possible to carry out isothermal annealing only 30-40 K below the glass transition temperature, beyond that noise to signal ratio in DSC increases extensively.

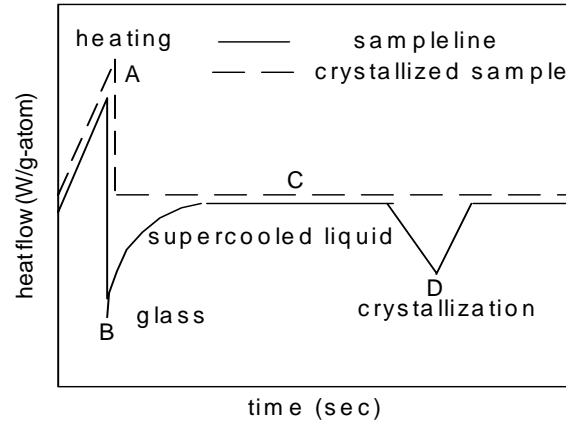


Figure 1. Schematic diagram of heat flow versus time depicts the relaxation from glassy state into the equilibrium supercooled liquid state when isothermally annealed below the glass transition temperature. The sample undergoes crystallization if held long enough in equilibrium supercooled liquid state. Solid line is indicative of sample run and dotted line represents the baseline run of the crystallized sample.

The sample is allowed to undergo relaxation by isothermal annealing in order to measure equilibrium enthalpy near the glass transition temperature. The Y-ordinate on the DSC scan represents the heat flux \dot{Q}^0 (J/sec) and is given by

$$\dot{Q}^0 = m \cdot c_p \cdot \dot{T} = \frac{dQ}{dt} \quad (1)$$

where, m = sample weight (mg), c_p = specific heat of the sample (J/g-atom K) and \dot{T} = the heating rate (K/s).

In enthalpy relaxation experiments, heat flow \dot{Q} is calculated by integrating heat flux over a period of time from the glassy state into the supercooled liquid state. The time at which relaxation starts from the glassy state is designated by t_{glass} and at times where material reaches the supercooled liquid state is designated by $t_{supercooled}$

$$Q = \int Q^0 = \int_{t_{glass}}^{t_{sup\ ercooled}} \frac{dQ}{dt} dt \quad (2)$$

where, Q^0 = Heat flow rate or heat flux (J/s), Q = Heat flow (J).

Being the extensive property, enthalpy is directly proportional to the quantity of the material in the system. To calculate the enthalpy, the heat flow Q is normalized by the sample weight and multiplied by the molecular weight of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ to obtain the enthalpy in J/g-atom. It is found that the relaxation process obeys stretched exponential function and it does not proceed exponentially with time [7]. Here the enthalpy relaxation is fitted with the stretched exponential function and enthalpy as a function of time is given by

$$H(t) = H_g - \Delta H_{total} \cdot (1 - e^{-(t/\tau)^\beta}) \quad (3)$$

where, τ = average relaxation time, β = a stretching exponent, t = time, H_g = enthalpy of the glass after relaxation, ΔH_{total} = total enthalpy change during relaxation from the glassy state into the equilibrium supercooled liquid state. After calculating the enthalpy change for all the isothermal runs carried out below the glass transition region enthalpy change is plotted as a function of time and two useful fitting parameters named relaxation time (τ) and stretching exponent beta (β) that help in predicting the glass forming ability of $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ are obtained by fitting with the stretched exponential function. Figure 2 shows the fitted curve of normalized enthalpy change $\Delta H/\Delta H_{(total)}$ versus time at a temperature of 661 K. The fitting equation is given by

$$\Delta H / \Delta H_{(total)} = 1 - e^{-(t/\tau)^\beta} \quad (4)$$

This equation is very similar to the equation 3 but for simplicity ΔH is normalized with respect to the total enthalpy difference $\Delta H_{(total)}$ on a scale of 0 to 1. Here we can say that enthalpy relaxes into the equilibrium supercooled liquid state because no crystal nuclei are formed on the time scale of experimental observation. The fitted curve yields relaxation time τ of 317 sec and stretched exponential function β of 0.88.

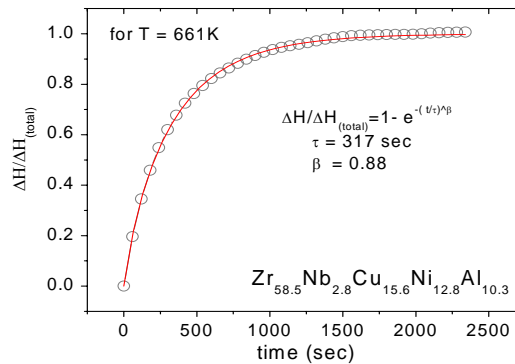


Figure 2. Illustration of curve fitting with stretched exponential function for temperature of 661 K that yields stretching exponent β of 0.88 and relaxation time τ of 317 sec.

Four examples of isothermal enthalpy relaxation fitted with the stretched exponential function are plotted in figure 3. It is seen from the plot that the enthalpy is increasing towards temperature away from the glass transition temperature e.g. 633 K. At the same time a longer time for relaxation is observed which is attributed to slow relaxation kinetics far from the glass transition temperature. On the contrary, gradual decrease in relaxation time and enthalpy towards the glass transition temperature e.g. 663 K are observed due to rapid kinetics and small initial departure from the equilibrium. The stretching exponent β is close to 0.79 far from the glass transition temperature and increases linearly towards the glass transition temperature. This indicates strong liquid behavior of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$, which is in contrast to typical fragile liquid having stretching exponent below 0.5 at the glass transition [8].

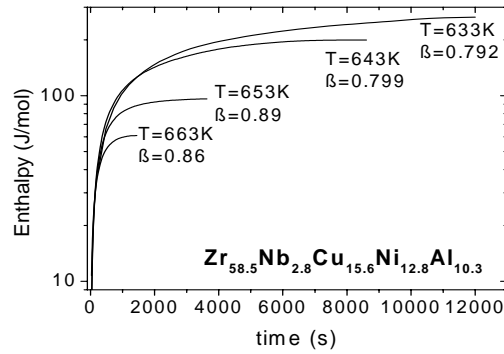


Figure 3. Isothermal enthalpy relaxation measurement as a function of time for four different temperatures. Stretched exponential function is used for fitting the data. β is the stretching exponent.

By fitting the enthalpy relaxation data it is found that the enthalpy relaxation is best fitted by Arrhenius relation rather than VFT on a plot of relaxation time τ versus inverse temperature ($1000/T$) as shown in figure 4. Arrhenius relation in terms of relaxation time is given by

$$\tau = \tau_0 \cdot \exp\left(\frac{Q}{RT}\right) \quad (5)$$

where, τ_0 is a pre-exponential constant, R is the gas constant, Q is the activation energy and T the absolute temperature. The fitted curve yields $\tau_0 = 4.5 \times 10^{-21}$ sec and Q of 2.97 eV.

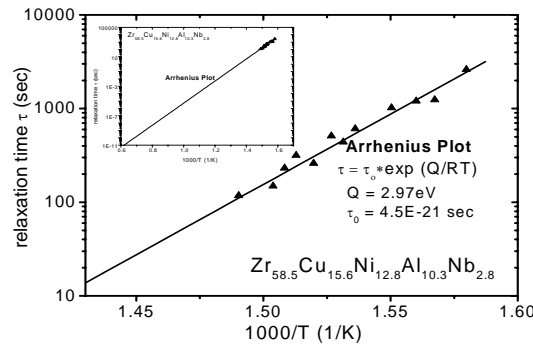


Figure 4. Arrhenius plot of the relaxation time of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ as a function of inverse temperature. Data are fitted with the Arrhenius relation. Q and τ_0 represent activation energy and pre-exponential constant respectively.

DISCUSSION

Time dependent relaxation phenomenon is not only important for improving basic understanding of the glass transition and transport phenomena but also essential for perceiving insight into technologically important properties such as damping, yield strength, ductile-to-brittle transition temperature, fracture toughness and fatigue crack growth rate in various glassy materials [9]. Supercooling the liquid in transformation range results in freezing of the liquid structure before the liquid relaxes towards the equilibrium. In order to reach the thermal equilibrium state from this structurally arrested non-equilibrium state of the liquid, annealing has been carried out in the transformation range. The amount of heat dissipated during this transition is a measure of the enthalpy of the sample and this process is known as enthalpy relaxation. According to the best of Author's knowledge, this is the first direct measurement of the enthalpy relaxation time scale in a metallic glass. Importance of the enthalpy relaxation process lies in its ability to contribute in understanding the liquid structure and indirectly the glass forming ability of bulk metallic glass forming alloy. In terms of free volume theory, annealing can reduce open volume regions, which are associated with the frozen-in structural state, and so does the excess free energy associated with it [10].

Residual enthalpy is frozen in as the liquid undergoes the glass transition. Upon isothermal annealing below the glass transition temperature, frozen enthalpy of the amorphous glass relaxes into the equilibrium supercooled liquid state as shown in figure 5. Increase in enthalpy difference ΔH between the glass and the supercooled liquid with decrease in temperature is shown in the plot.

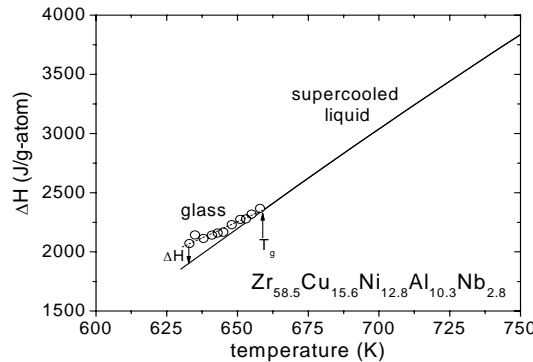


Figure 5. Enthalpy change between glass and supercooled liquid state as a function of temperature. (○) shows the actual data points from the enthalpy relaxation experiments below the glass transition temperature. Downward arrow indicates enthalpy difference ΔH between these two states.

For $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$, Arrhenius expression describes the enthalpy relaxation time better than a VFT relation for isothermal relaxation experiments. The time scale for the enthalpy relaxation follows the time scale for diffusive processes. Considering this diffusive process in terms of atomic motion it is found that for Zr-Ti-Cu-Ni-Be, at higher temperature above T_g , relaxation time scales are associated with the large-scale cooperative motion of groups of atoms. Instead at lower temperatures in the proximity of T_g , relaxation is well described by the local

adjustment in atomic positions [9,11] or collective hopping mechanism. It is likely to control the diffusion of medium sized (Al, Nb) and small sized (Cu, Ni) atoms in our BMG alloy. It was reported for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ that medium sized atom such as Ni is likely to diffuse by the collective hopping mechanism in the deeply supercooled liquid state [11]. The collective hopping mechanism for the medium sized atom such as Co is confirmed by isotope effect measurements in case of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ [12]. Activation energy obtained by fitting the enthalpy relaxation data is analogous to the activation energy required for the diffusion of aluminum at lower temperatures. Hence, solid-state diffusion at lower temperatures is mainly governed by the activated jumps of medium sized Al and Nb atoms. Yet, further experiments including quasielastic neutron scattering is essential to confirm this results.

CONCLUSION

Kinetic behavior of $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$ bulk metallic alloy was studied below the glass transition region using DSC. An experimental method is developed to study the enthalpy relaxation behavior. The relaxation time best fitted with Arrhenius relation suggests that enthalpy relaxation is controlled by the solid-state diffusion of constituent alloy. The activation energy is comparable with the activation energy of constituent metallic elements. It is believed that the motion of the medium sized atoms of this alloy, which are likely to diffuse by the collective hopping mechanism, govern the relaxation in the proximity of glass transition temperature.

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